Single-step Sulfur Recovery Process (SSRP)

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The direct catalytic oxidation of H_2S in the presence of great excess (> 60%) H_2 and CO was examined on a commercial alumina catalyst at 125-160°C and 200-350psig. Total sulfur (H_2S + SO_2) conversions of 98.5% or higher were achieved, with the undesirable formation of carbonyl sulfide limited to below 40ppm. SO_2 is much more selective than oxygen for the catalytic oxidation of H_2S to high-purity sulfur by the Single-step Sulfur Recovery Process (SSRP).

INTRODUCTION

Gasification of heavy feeds (e.g., coal, pet coke, resid, biomass) produces a raw fuel gas that requires cleaning before its use to produce electricity and/or synthetic liquid fuels (e.g., using Fischer-Tropsch synthesis). The current commercial process for gas cleaning involves quenching the gas to remove particulates and trace contaminants. Then, a complex multi-step amine-based process to remove hydrogen sulfide (H_2S) follows. The fuel gas is first contacted by an amine solution using a gas-liquid scrubber. The spent amine is then regenerated using steam and the regeneration off-gas containing H_2S is sent to a Claus plant. An H_2S burner oxidizes 1/3 of H_2S to SO_2, which then reacts with the remaining H_2S to form sulfur:

$$2\ H_2S + SO_2 \rightarrow 3/n\ S_n + 2\ H_2O \qquad \text{(Claus reaction)}$$
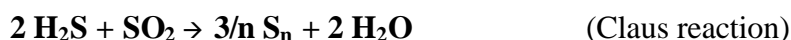
The Claus reaction uses a series of up to three catalytic reactors, and yet its tail gas still contains about 2% of the inlet $H_2S – SO_2$ mixture, which is then sent to a tail gas treatment plant. To reduce the numerous steps in conventional sulfur removal and recovery processes, RTI with DOE/NETL funding is developing the **Single-step Sulfur Recovery Process (SSRP)**. The SSRP consists of injecting SO_2 directly into the quenched fuel gas to oxidize H_2S selectively on a suitable catalyst to both remove and recover sulfur in a single step. The key differences between SSRP and the traditional Claus process are: a) in SSRP the catalytic oxidation of H_2S by SO_2 (Claus reaction) occurs selectively in a highly reducing atmosphere containing the highly reactive H_2 and CO fuel gas components, and b) the reaction is carried out at the pressure of the fuel gas (300-1200 psig). The temperature of the SSRP reactor is within 125°C (257°F, where sulfur liquefies) and 160°C (320°F, where liquid sulfur viscosity starts to increase rapidly). The SSRP uses a catalyst that is highly selective for the oxidation of H_2S as opposed to the undesirable oxidation of H_2 and CO that are present in great excess in the fuel gas (ca. 60vol% vs. less than 1vol% H_2S).

A review of the literature did not identify any studies in which the Claus reaction was carried out in the presence of large concentrations of CO and H_2. Pearson (1976) studied the Claus reaction at temperatures between 135°C and 175°C using a Claus tail gas containing ca. 3vol% CO+H_2. Conversion of H_2S+SO_2 was 96 to 98% until his active alumina catalyst reached 60% sulfur loading in the pores. The conversion then declined rapidly to 31%.

The scope of this work is to determine the feasibility of the SSRP for the selective catalytic oxidation of H_2S in the presence of excess amounts (> 30vol%) of highly reactive gases such as H_2 and CO. Also, it is to evaluate the performance of commercial catalysts to selectively remove and recover high-purity sulfur under commercially applicable process conditions.

EXPERIMENTAL

The SSRP reaction was studied in a 0.5-inch fixed-bed micro-reactor at 125-160°C (257-320°F) and 200-350 psig, over a commercial high-surface-area ($227m^2$/g) alumina catalyst. The stainless steel reactor was coated with silica to minimize reactions on its walls. The reactant feed consisted of a simulated Texaco coal gas stream containing 50.8% CO, 35.7% H_2, 12.5% CO_2, and 1.0% H_2S, and a 2.5% SO_2/N_2 stream. A syringe pump provided a constant flow of steam (through water evaporation) into the coal gas line. A typical reaction composition included ca. 8400ppm H_2S, ca. 4200ppm SO_2, 10% steam, and a balance of simulated Texaco gasifier gas (N_2, CO_2, H_2, and CO). The steam condensed into a condensation pot past the reactor outlet. A back-pressure-control valve, located downstream of the condenser, controlled the reactor and condenser pressure. The outlet gases were analyzed in a gas chromatograph with a thermal conductivity detector (TCD) and a flame photometric detector (FPD), for high (above 500ppm) and low (down to single-digit ppm) sulfur-gas concentrations, respectively. A schematic of the SSRP reaction system is shown in Figure 1.
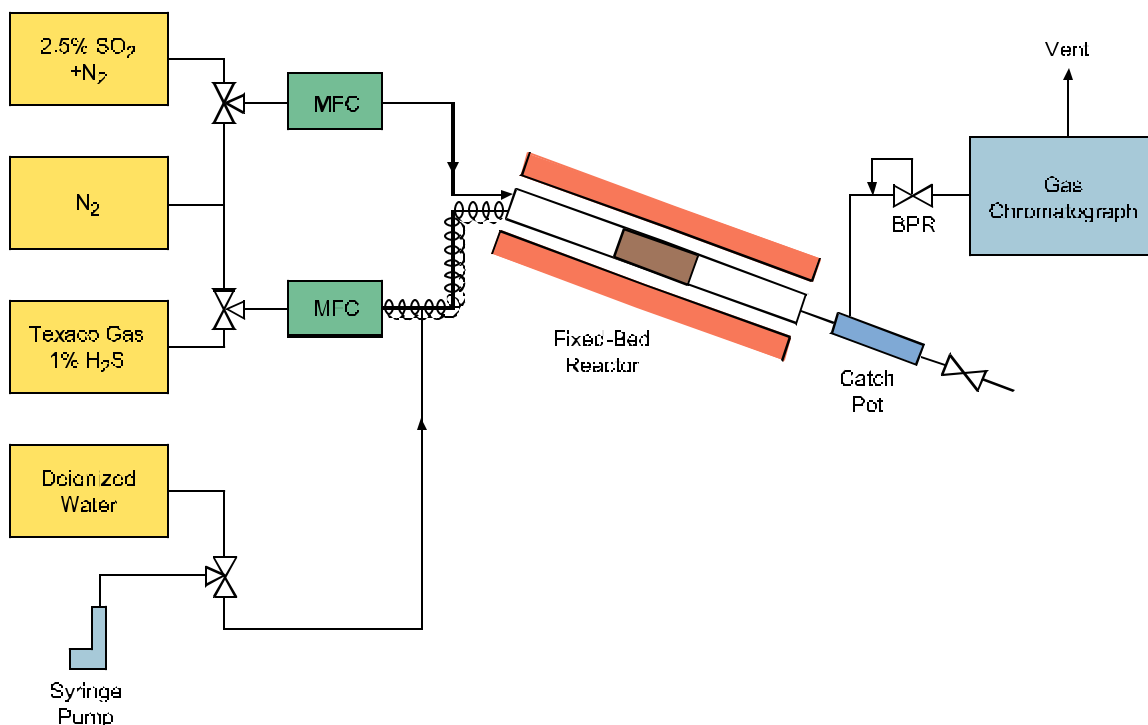

Figure 1. Schematic of the SSRP reaction system

RESULTS AND DISCUSSION

The SSRP reaction experiments were conducted by loading the silica-coated reactor with 5 cm^3 of alumina catalyst, then heating to 154°C (309°F) and pressurizing to 200psig (14.4 bar) under an inert gas flow of 100sccm. 15sccm SO_2/N_2 (corresponding to ca. 3800ppm SO_2) were fed into the reactor, followed by feeding 10sccm steam, substituting an equal flow of N_2. Upon reaching a pseudo steady state, simulated coal gas with H_2S was fed into the reactor (giving ca. 8400ppm H_2S), at a constant total feed flow of 100sccm. The total sulfur (H_2S+SO_2) conversion was 86.5%, with less than 20ppm COS (carbonyl sulfide) formation.

The effect varying the inlet SO_2 concentration was examined by increasing the SO_2/N_2 flow from 15 to 18 to 20sccm while keeping the coal gas and steam flows constant, thus increasing the total flow from 100 to 103 to 105sccm, respectively. The results are shown in Figure 2. Upon increasing the SO_2 inlet concentration the conversion of H_2S increased up to 99.5%, while the conversion of SO_2 decreased from essentially 100% down to ca. 87%. Thus the H_2S+SO_2 conversion showed a maximum at an intermediate SO_2 concentration. This implies reaction of SO_2 with H_2S only, and not with H_2 or CO which are in great excess, at least to any appreciable rate. The COS formation was only about 20ppm.

The effect of space velocity was studied by varying the total feed flow from 100sccm to 500sccm while keeping the other reaction parameters (temperature, pressure, feed composition) constant. A fivefold increase in space velocity resulted in only a minor decrease (from 98.5% to 96%) in H_2S+SO_2 conversion (Figure 3). The formation of COS was again only about 20ppm. Thus the SSRP reaction is very active and selective even at significantly small contact times.
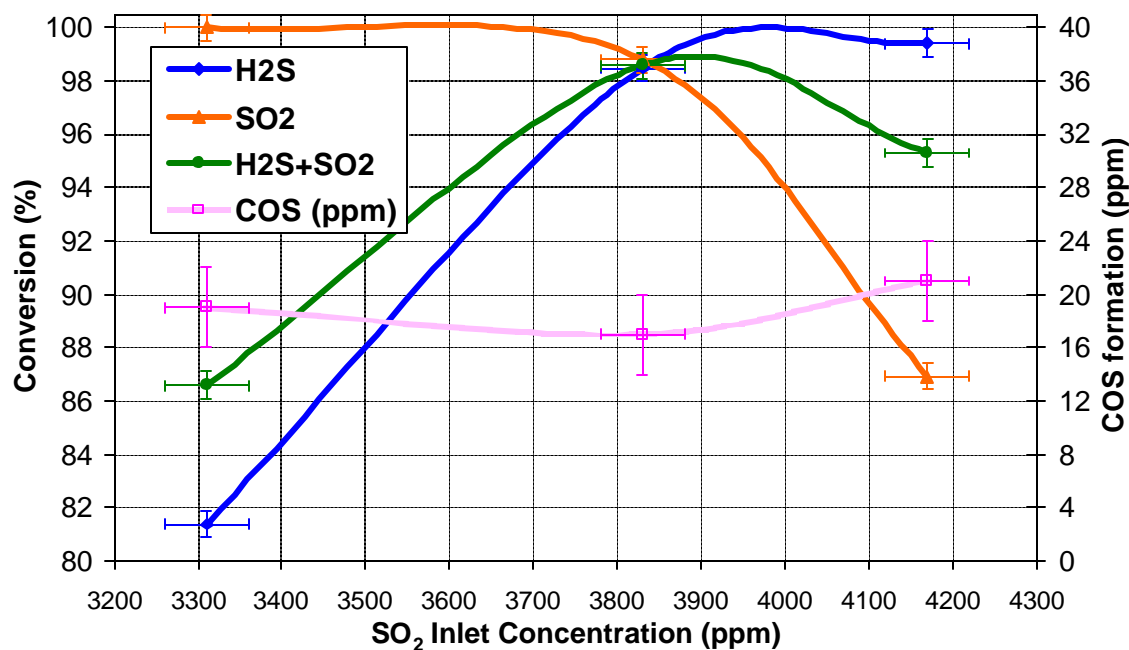

Figure 2. Effect of SO_2 inlet concentration on H_2S, SO_2, and H_2S+SO_2 conversion, and COS formation, for SSRP on alumina; T: 154°C, P: 200psig; SV: 1200 (1230) (1260) h^{-1}; H_2S: 8400-8000ppm; steam: 10%
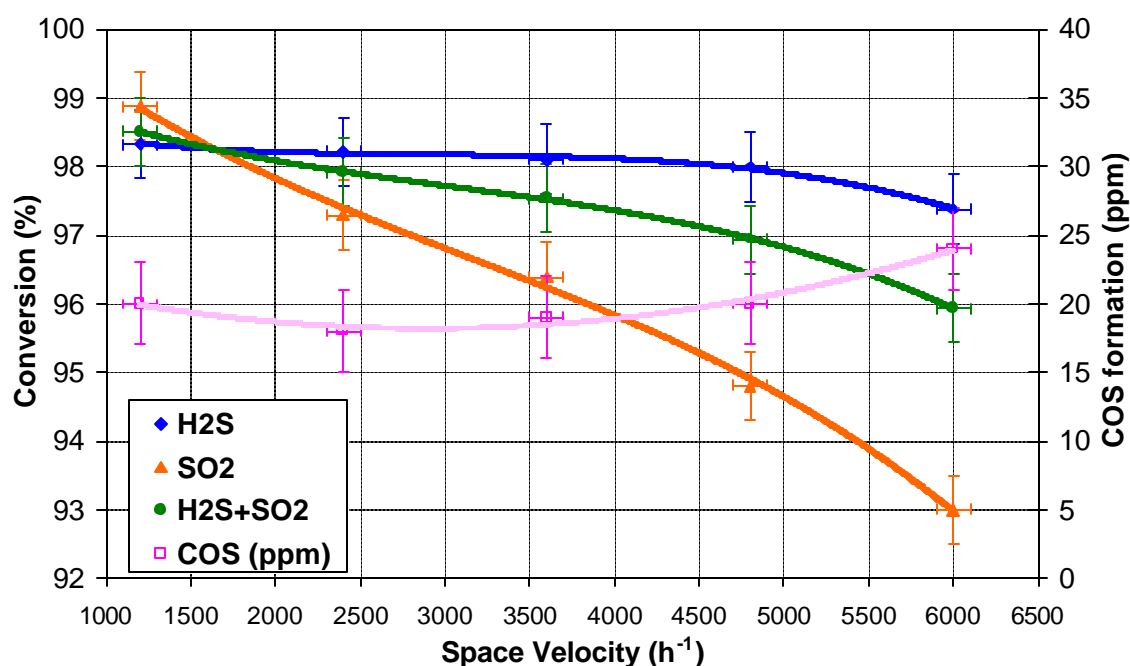
Figure 3. Effect of space velocity on H_2S, SO_2, and H_2S+SO_2 conversion, and COS formation, for SSRP on alumina; T: 154°C, P: 200psig; H_2S: 8400pm; SO_2: 4200ppm; steam: 10%

The effect of pressure was examined by increasing the reaction pressure from 200psig (12.4 bar) to 350psig (25.8 bar) at a total feed flow of 300sccm while keeping the other reaction parameters (temperature, feed composition) constant. The results are given in Table 1. The combined H_2S+SO_2 conversion was found to increase up to 99.0%. Higher pressures favor the reaction in terms of thermodynamic equilibrium, so they would be expected to further increase the measured conversion. The amount of formed COS was below 40ppm.

Table 1. Effect of pressure on H_2S, SO_2, and H_2S+SO_2 conversion, and COS formation, for SSRP on alumina; T: 154°C, H_2S: 8400ppm; SO_2: 4200ppm; steam: 10%

Pressure (psig)	Conversion (%)			COS formation (ppmv)
	H_2S	SO_2	H_2S+SO_2	
200	98.9	97.3	98.4	34
240	98.9	98.4	98.7	34
300	99.0	99.0	99.0	36
350	98.8	99.3	99.0	38

The effect of catalytically oxidizing H_2S in the presence of excess H_2 and CO by an oxidant other than SO_2 (such as O_2) was also examined on alumina at 154°C, 200psig, and a total flow of 100sccm. After addition of 10% steam for 30min, $2\%O_2/N_2$ was fed into the reactor,

producing ca. 4300ppm O_2 in the feed, at a total flow of 105sccm. Then, coal gas was fed to get a ratio of H_2S/O_2 of ca. 2 and the reaction reached a pseudo steady state. Finally, the O_2 flow was substituted by a flow of SO_2 producing ca. 4300ppm of SO_2 in the feed (H_2S/SO_2 ratio of ca. 2) and the reaction reached a new pseudo steady state.

The results for the effect of O_2 vs. SO_2 in the feed are given in Figure 4. Oxygen is much less selective for the oxidation of H_2S compared to SO_2 and also allows for enhanced undesirable formation of COS. There appears to be a clear unselective consumption of O_2 by the H_2 and/or CO of the coal gas, thus limiting its availability for the desirable selective reaction with H_2S.

The sulfur that was generated on the catalyst during the SSRP was retained within the catalyst pores (the collected water condensate was clear). Normally in low temperature fixed-bed Claus-type processes, the catalyst is reversibly poisoned by the sulfur plugging its pores, as shown by Pearson (1975). The catalyst would have to be heated to high temperatures to remove the sulfur.

A commercial embodiment of the SSRP involving a liquid phase of molten sulfur with dispersed catalyst in a slurry bubble column reactor (SBCR) is currently under development (Gangwal et al, 2002). A schematic of this embodiment is given in Figure 5. The sulfur that is generated during the SSRP dissolves into the molten sulfur, in analogy to the wax formed and removed by the liquid wax medium in a slurry-bubble column Fischer-Tropsch reactor. Therefore, recovery of the product sulfur as well as a shift in thermodynamic equilibrium limitations on sulfur formation can be accomplished.
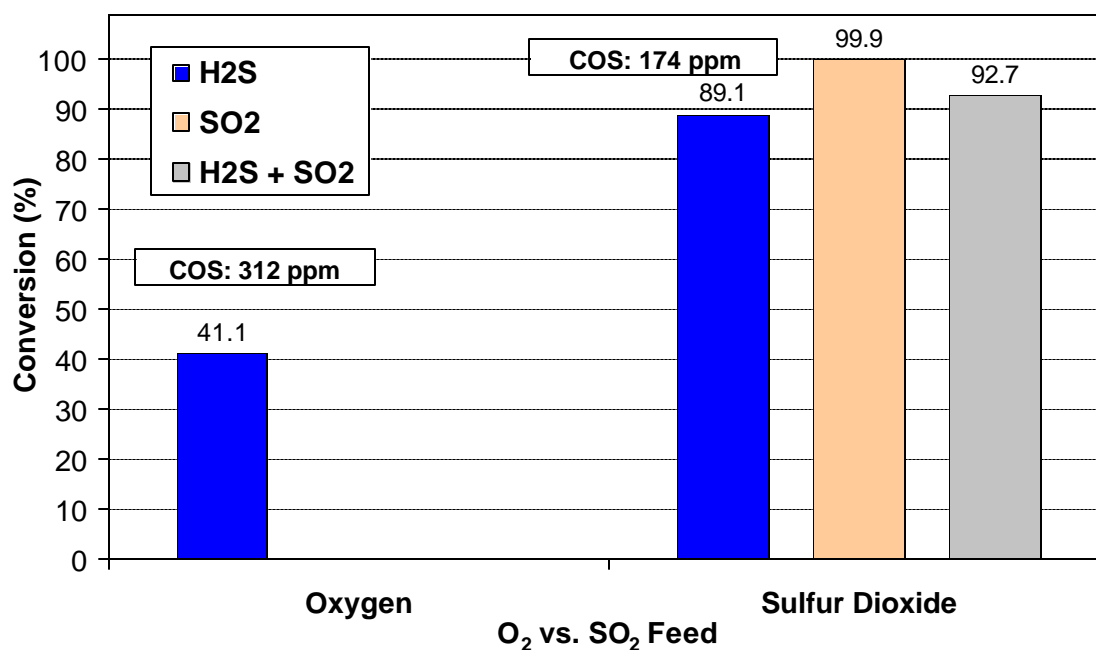

Figure 4. Effect of O_2 vs. SO_2 feed on H_2S, SO_2, and H_2S+SO_2 conversion, and COS formation, for SSRP on alumina; T: 125°C, P: 200psig; H_2S: 8400pm; O_2 (SO_2): 4300ppm; steam: 10%
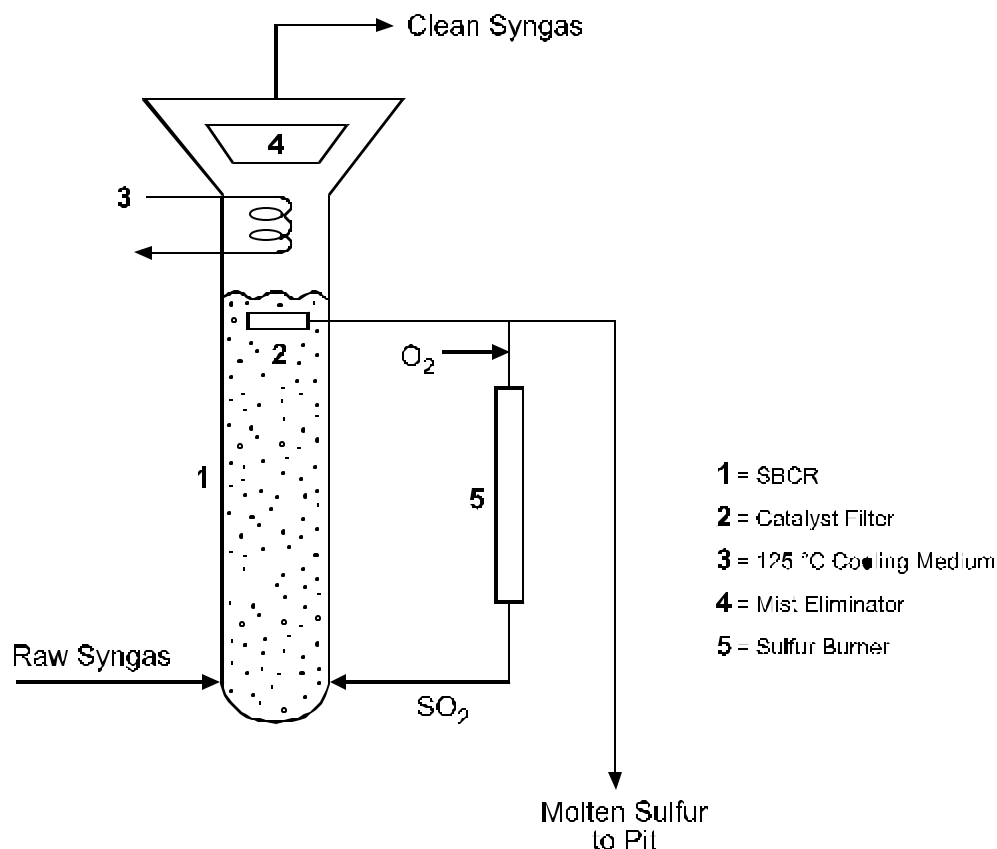
Figure 5. Proposed commercial embodiment of the Single-step Sulfur Recovery Process (SSRP)

CONCLUSIONS

The results of this work have clearly demonstrated that the direct catalytic oxidation of H_2S by SO_2 can be successfully performed even in the presence of great excess of highly reactive reducing species such as H_2 and CO. The combined H_2S+SO_2 conversion on an alumina catalyst is 98.5% at 154°C and 200psig and further increases with increasing pressure (99% at 300psig), being limited only by thermodynamic equilibrium from attaining 100%. Furthermore, higher pressures would shift the equilibrium limitations towards higher conversion, thus the SSRP is favored by using high-pressure fuel gas (300-1200psig). SO_2 is a much more selective oxidant compared to oxygen for selectively oxidizing H_2S in the presence of excess H_2 and CO. Under the examined experimental conditions, the undesirable formation of COS was limited to 40ppm or lower.

REFERENCES

Gangwal, S.K., Nikolopoulos, A.A., and Dorchak, T.P., "Method of Removing and Recovering Elemental Sulfur from Highly Reducing Gas Streams Containing Sulfur Gases", US Patent applied for, July 2002.

Pearson, M.J., "Catalyst Performance in Low-Temperature Claus Process", Energy Processing/ Canada, July-August 1976, 38-42.